

Article

Synthesis and Characterization of Heptacoordinated Tin(IV) Complexes.**X-ray Crystal Structure of $[n\text{Bu}_2\text{Sn}(\text{dappt})] \cdot (\text{Me}_2\text{CO})_{0.5}$ [H_2dappt = 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone)]****Gerimário F. de Sousa^{a*}, Victor M. Deflon^a, Elke Niquet^b and Anuar Abras^c**^a*Instituto de Química, Universidade de Brasília, 70919-970, Brasília - DF, Brazil*^b*Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076, Tübingen, Germany*^c*Departamento de Física, Universidade Federal de Minas Gerais, 30123-970, Belo Horizonte - MG, Brazil*

As reações do ligante 2,6-diacetilpiridina *bis*(4-feniltiossemicarbazona), H_2dappt , com $\text{R}_{4-m}\text{SnX}_m$ ($m = 2, 3$; $\text{R} = \text{Me}, n\text{Bu}, \text{Ph}$ e $\text{X} = \text{Cl}$) resultaram na formação de quatro novos complexos organoestânicos heptacoordenados, os quais foram caracterizados por análise elementar e pelas espectroscopias no IV e Mössbauer. O derivado *n*-butila, $[n\text{Bu}_2\text{Sn}(\text{dappt})] \cdot (\text{Me}_2\text{CO})_{0.5}$, foi também analisado por um estudo de difração de raios X em um monocristal. O complexo cristalizou-se no sistema monoclínico e grupo espacial C2/c, com $a = 36,164(14)$, $b = 9,7050(15)$, $c = 26,194(11)$ Å, $\beta = 132,00(2)^\circ$, $Z = 8$. A determinação da estrutura revelou um complexo neutro de Sn(IV), numa geometria bipiramidal pentagonal (BPP), com o plano equatorial definido pelos átomos doadores SNNNS do ligante e dois grupos *n*-butila nas posições axiais. Também é discutida uma correlação entre os dados de Mössbauer e de difração de raios X, baseada no modelo da carga-pontual.

The reactions of the 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone) ligand, H_2dappt , with $\text{R}_{4-m}\text{SnX}_m$ ($m = 2, 3$; $\text{R} = \text{Me}, n\text{Bu}, \text{Ph}$ and $\text{X} = \text{Cl}$) led to the formation of four new heptacoordinated organotin(IV) complexes, which were characterized by microanalyses and by IR and Mössbauer spectroscopies. The *n*-butyl derivative $[n\text{Bu}_2\text{Sn}(\text{dappt})] \cdot (\text{Me}_2\text{CO})_{0.5}$ was also analyzed by a single crystal X-ray diffraction study. It crystallized in the monoclinic system with a space group C2/c, with $a = 36.164(14)$, $b = 9.7050(15)$, $c = 26.194(11)$ Å, $\beta = 132.00(2)^\circ$, $Z = 8$. The structure determination revealed a neutral complex of Sn(IV) in a distorted pentagonal bipyramidal (PBP) geometry, with the equatorial plane defined by the SNNNS donor system of the ligand and with the two *n*-butyl groups in the axial positions. Also, a correlation between Mössbauer and X-ray data based on the point-charge model is discussed.

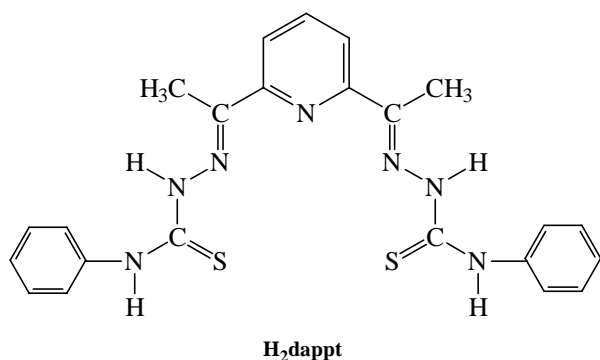
Keywords: thiosemicarbazone complexes, heptacoordinated organotin(IV) complexes, X-ray diffraction analysis

Introduction

The chelating properties of 2,6-diacetylpyridine *bis*(thiosemicarbazones) have been investigated and six different coordination modes have been discovered so far. $[\text{Ph}_2\text{Sn}(\text{daptsc})] \cdot 2\text{DMF}^1$ (H_2daptsc = 2,6-diacetylpyridine *bis*(thiosemicarbazone), which was obtained from Ph_2SnO in DMF (N,N-dimethylformamide), crystallizes in a regular PBP geometry with the dianion daptsc^{2-} in the pentagonal plane and the two phenyl groups in the axial positions. Similarly, in $[n\text{Bu}_2\text{Sn}(\text{H}_2\text{daptsc})]\text{Cl}_2 \cdot \text{MeNO}_2^2$ the Sn(IV) atom is heptacoordinated in a distorted PBP configuration, with the five SNNNS donor atoms of the H_2daptsc in the pentagonal plane. In $[\text{Ph}_2\text{Sn}(\text{Hdaptsc})]\text{Cl}^3$ the Sn(IV) atom is heptacoordinated and also has a PBP geometry, where only

one of the H_2daptsc arms has undergone deprotonation. A fourth coordination mode was reported for $[\text{Zn}_2(\text{daptsc})_2] \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}^4$, where each of the two fully deprotonated ligands, daptsc^{2-} , are coordinated to two Zn(II) atom in a distorted octahedral geometry. The dinuclear complex $[\text{Zn}_2(\text{daptsc})_2] \cdot \text{MeOH} \cdot \text{H}_2\text{O}^4$, crystallized from MeOH solution, possesses one octahedral and one tetrahedral Zn(II) atoms. Finally, spectroscopic and X-ray studies showed that *bis*(thiosemicarbazones) can also behave as tetradentate dianionic ligands, forming square-planar complexes with Ni(II), Cu(II) and Pd(II) in the sixth coordination mode⁵. In this case, the metal ion is coordinated through the pyridine nitrogen, the thiolate sulfur, the azomethine nitrogen and the thioimide nitrogen atom. The other sulfur atom remains in the thione form and does not coordinate.

Since both Sn(IV)⁶ and thiosemicarbazones⁷ have significant pharmacological activity, some crystal structures of organotin(IV) complexes with 4-substituted thiosemicarbazones have already been discussed⁶. We report in this work the preparation and characterization of new heptacoordinated organotin(IV) complexes with the ligand 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone), whose structure is shown below.



Experimental

Materials

All solvents were purified and dried according to standard procedures. 2,6-diacetylpyridine (Aldrich) and the organotin halides (Aldrich) were used without further purification. IR spectra were recorded on a Nicolet 5ZDX-FT spectrophotometer in the 4000–400 cm⁻¹ range using KBr pellets. ¹¹⁹Sn Mössbauer spectra were recorded using a constant acceleration spectrometer moving a CaSnO₃ source at room temperature. The samples were analyzed at 85K. The spectra were computer-fitted, assuming Lorentzian lines shapes. X-ray diffraction data were collected at room temperature using an Enraf-Nonius CAD-4 automatic diffractometer, with a graphite monochromated MoK_α radiation obtained in a fine focus sealed tube (see Table 1).

Preparation of H₂dappt and its Sn(IV) complexes

The pale yellow 2,6-diacetylpyridine *bis*(4-

Table 1. Crystal data, data collection and structure refinement parameters for [Bu₂Sn(dappt)]·(Me₂CO)_{0.5} (**3**).

Formula		C _{32.5} H ₄₂ N ₇ O _{0.5} S ₂ Sn
Formula weight (g mol ⁻¹)		721.54
Crystal system		monoclinic
Crystal color		orange
Formula units	Z	8
Space group		C2/c
Crystal dimensions (mm ³)		0.40 x 0.40 x 0.10
Temperature (K)	T	293(2)
Cell constants (Å, °)	a	36.164(14)
	b	9.7050(15)
	c	26.194(11)
	β	132.00(2)
Volume (Å ³)	V	6832(4)
Calculated density (g cm ⁻³)	ρ _x	1.403
Range of data collection	θ	3–27°
	h k l	–1 → 46, 0 → 12, –33 → 25
F(000)		2976
Absorption coefficient (mm ⁻¹)	μ	0.905
Radiation		Mo-K _α
Wavelength (Å)	λ	0.71073
Collected reflections		7813
Unique reflections/R(int)		7458/0.0255
Observed reflections {I > 2σ(I)}		5739
Absorption correction		Ψ-Scan ¹⁰
Min./max. Transmission		0.80698/0.95784
Structure solution		heavy atom method ¹¹
Refinement method		full-matrix least-squares on F ² ¹²
Parameters refined		338
Goodness-of-fit	S	1.016
Final structure factors {I > 2σ(I)}	R1	0.0430
	wR2	0.1125

phenylthiosemicarbazone), H_2dappt , was prepared by refluxing a 2:1 molar mixture of 4-phenylthiosemicarbazide⁸ with 2,6-diacetylpyridine in absolute EtOH. The Sn(IV) complexes were obtained by the following procedure: 0.097 g (0.21 mmol) of H_2dappt were dissolved by refluxing a 1:1 molar mixture of MeOH/Me₂CO (10 mL) for 10 min. To this solution was added 0.22 mmol of the appropriate organotin(IV) species, dissolved in 2 mL of MeOH, and the resulting mixture was refluxed for about 1 h. Cooling the solution and slow evaporation of the solvent led to the appearance of crystalline products with yields on the order of 60%. The microanalyses were performed with a Perkin Elmer 2400C analyzer, giving for C, H and N the following results.

H_2dappt . Anal. Found: C, 59.05; H, 4.82; N, 21.24. Calcd. for C₂₃H₂₃N₇S₂: C, 59.87; H, 4.99; N, 21.26%.

1. MeSnCl($dappt$), m.p. 157 °C (dec.). Anal. Found: C, 47.22; H, 3.68, N, 15.51. Calcd. for C₂₄H₂₄ClN₇S₂Sn: C, 45.85, H, 3.85, N, 15.59%.

2. [Me₂Sn($dappt$)], m.p. 231-234 °C. Anal. Found: C, 48.60; H, 4.39, N, 15.97. Calcd. for C₂₅H₂₇N₇S₂Sn: C, 49.36; H, 4.47; N, 16.12%.

3. [ⁿBu₂Sn($dappt$)]·(Me₂CO)_{0.5}, m.p. 238-241 °C. Anal. Found: C, 53.58; H, 5.64, N, 13.53. Calcd. for C_{32.5}H₄₂N₇O_{0.5}S₂Sn: C, 52.77; H, 5.48; N, 14.13%.

4. [Ph₂Sn($dappt$)], m.p. 134 °C (dec.). Anal. Found: C, 48.03; H, 3.71; N, 9.24. Calcd. for C₃₅H₃₁N₇S₂Sn: C, 49.11; H, 3.74; N, 8.53%.

Results and Discussion

Crystal and molecular structure of [ⁿBu₂Sn($dappt$)]·(Me₂CO)_{0.5} (**3**).

The ORTEP drawing of the molecular structure of di-*n*-butyl[2,6-diacetylpyridine bis(4-phenylthiosemicarbazone)]tin(IV) acetone solvate, [ⁿBu₂Sn($dappt$)]·(Me₂CO)_{0.5} (**3**), is shown in Figure 1. Crystal structure parameters and conditions of data collection are given in Table 1. Selected bond distances and angles are presented in Table 2.

All non hydrogen atoms were refined with anisotropic displacement parameters with the exception of those of the *n*-butyl groups and those of the solvate molecule. For the latter, greater freedom for thermal displacements was observed in accord with their low steric hindrance. The hydrogen atoms were fitted on idealized positions.

The *n*-butyl group bonded to Sn(IV) *via* C(31) shows considerably greater displacement parameters than the other one. This should be related to thermal movements. The second butyl group is proximate to the solvate

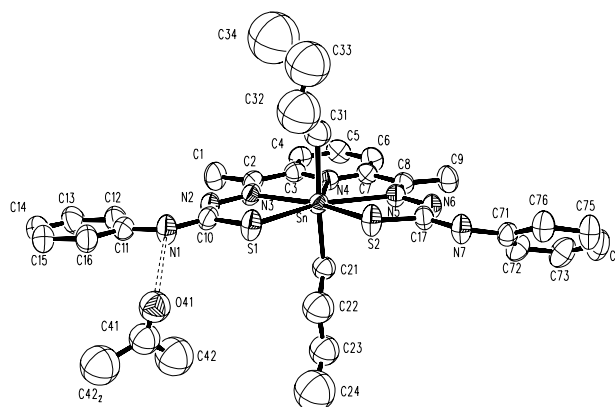


Figure 1. Ellipsoid representation⁹, with labeled atoms and 50% probability, of the asymmetric unit of [ⁿBu₂Sn($dappt$)]·(Me₂CO)_{0.5} (**3**). For the sake of clarity the hydrogen atoms are omitted.

Table 2. Selected bond distances (Å) and angles (°) for [ⁿBu₂Sn($dappt$)]·(Me₂CO)_{0.5} (**3**). Standard deviation in parentheses.

Sn-C(21)	2.148(4)	C(2)-N(3)	1.292(5)
Sn-C(31)	2.155(5)	C(3)-N(4)	1.348(5)
Sn-N(3)	2.450(3)	C(7)-N(4)	1.338(5)
Sn-N(4)	2.411(3)	C(8)-N(5)	1.292(5)
Sn-N(5)	2.465(3)	C(10)-N(2)	1.306(5)
Sn-S(1)	2.6210(17)	C(17)-N(6)	1.309(5)
Sn-S(2)	2.6878(15)	C(10)-N(1)	1.372(5)
N(2)-N(3)	1.374(4)	C(17)-N(7)	1.366(5)
N(5)-N(6)	1.374(4)	C(10)-S(1)	1.740(4)
N(1)-O(41)	2.937(4)	C(17)-S(2)	1.738(4)
N(1')-O(41)	2.937(4)	N(7)-S(2)''	3.686(4)
C(21)-Sn-C(31)	168.12(18)	N(4)-Sn-S(1)	138.30(8)
C(21)-Sn-N(4)	84.78(14)	N(4)-Sn-S(2)	137.05(8)
C(31)-Sn-N(4)	83.56(16)	N(3)-Sn-S(1)	72.05(9)
C(21)-Sn-N(3)	88.59(14)	N(5)-Sn-S(2)	70.87(8)
C(31)-Sn-N(3)	88.82(16)	N(5)-Sn-S(1)	155.25(8)
C(21)-Sn-N(5)	85.16(14)	N(3)-Sn-S(2)	156.55(8)
C(31)-Sn-N(5)	88.07(16)	S(1)-Sn-S(2)	84.62(4)
N(4)-Sn-N(5)	66.36(11)	C(10)-S(1)-Sn	99.85(15)
N(4)-Sn-N(3)	66.26(11)	C(17)-S(2)-Sn	99.75(14)
N(3)-Sn-N(5)	132.56(11)	C(7)-N(4)-Sn	119.9(2)
C(21)-Sn-S(1)	94.06(12)	C(3)-N(4)-Sn	120.1(3)
C(31)-Sn-S(1)	96.16(14)	C(8)-N(5)-Sn	120.1(3)
C(21)-Sn-S(2)	95.49(12)	N(2)-N(3)-Sn	123.9(2)
C(31)-Sn-S(2)	91.48(15)	N(6)-N(5)-Sn	124.3(2)
N(1)-H(1)···O(41)	138.5	N(7)-H(7)···S(2)''	161.1

Symmetry transformations: $-x + 1, y, -z + \frac{1}{2}$; $-x + 1, -y + 2, -z + 1$.

molecule, resulting in additional constraints on its freedom. The carbon atom C(33) was found close to C(32) and too far from C(34), with unrealistic interatomic distances for both C(32)-C(33) and C(33)-C(34) bonds that were then restrained to have similar values, as expected.

The single crystal X-ray diffraction studies revealed the occurrence of a heptacoordinated neutral complex of approximately pentagonal bipyramidal (PBP) geometry, with the organic ligand lying in the equatorial plane. The approximate coplanarity between the phenyl rings and the bipyramidal equatorial plane suggests electron delocalization along the equatorial atoms. The mean deviation from planarity for the dappt²⁻ atoms is 0.077 Å, except for the side methyl groups and the N-phenyl groups that were not fitted. The Sn(IV) atom has a deviation of 0.046(1) Å from this plane. The angle between the equatorial plane and the phenyl ring attached to the nitrogen atom N(1) is 6.8(1)°. The other phenyl group, bound to N(7), is somewhat more twisted, with a torsion angle of 36.5(1)°.

Due to geometrical requirements of the thiosemicarbazone structure the pentagon is not regular. The S(1)-Sn-S(2) angle is significantly larger [84.62(4)°] than that of a regular pentagonal bipyramide (72°), while the other equatorial angles involving the Sn(IV) atom are in the 66.25(11)° - 72.05(9)° range. The axial *n*-butyl groups contribute to the distortion of the bipyramide structure since the C(21)-Sn-C(31) angle is 168.12(18)°.

The Sn-S and Sn-N bond distances, which average 2.654 and 2.442 Å, respectively, are in good agreement with the values (Sn-S = 2.593 - 2.692; Sn-N = 2.417 - 2.436 Å) found in two other heptacoordinated pentagonal bipyramidal diorganotin(IV) complexes containing a pentadentate thiosemicarbazone in the equatorial plane, namely [ⁿBu₂Sn(Achexim)]² and [Ph₂Sn(daptscl)]·2DMF¹ [H₂Achexim = 2,6-diacetylpyridine *bis*(3-hexamethyleimineylthiosemicarbazone) and H₂daptscl = 2,6-diacetylpyridine *bis*(thiosemicarbazone)]. However, these distances are considerably longer than the corresponding bonds Sn-S = 2.5425(8) and Sn-N(3) = 2.199(2) Å in the trigonal bipyramidal (TBP) complex, [Me₂Sn(L)]⁶ (H₂L = salicylaldehydethiosemicarbazone), as would be expected from the structural differences between the ligands and the consequent different hybridizations of the Sn(IV) atom in each complex. The Sn-C distances in the three heptacoordinate complexes are quite similar and evidently insensitive to the different nature of the s-bonded organic groups.

Due to the deprotonation of the hydrazine nitrogen atoms, N(2) and N(6), a delocalization of the negative charges along the N(3)-N(2)-C(10)-S(1) and N(5)-N(6)-C(17)-S(2) atoms is in agreement with the shortening of the following bond distances N(2)-C(10) = 1.306(5) and N(6)-C(17) = 1.309(5) Å, thus confirming the N-C double bond character. As a result of the thiolate sulfur coordination, the C(10)-S(1) = 1.740(4) and C(17)-S(2) = 1.738(4) Å bonds lose their π-character, becoming essential, single bonds.

The solvate acetone carbonyl C(41) and O(41) atoms occupy special positions so that the C=O bond coincides with the two fold rotation axis. The oxygen O(41) atom participates through its free electron pairs in two hydrogen bonds with neighboring complex molecules *via* the nitrogen N(1) atom. The N(1)···O(41) distance [2.937(4) Å] is in good agreement with the normally observed distance for this type of bond (2.93 Å)¹³. The N(1)-H(1)···O(41) angle [138.5°] shows appreciable deviation from linearity. Hydrogen bonds are also observed between the N(7) and S(2) atoms, of two neighboring molecules, as shown in Figure 2. The N(7)···S(2)'' distance [3.686(4) Å] is in this case 0.34 Å longer than the sum of the van der Waals radii of the two atoms (3.35 Å)¹³ and the N(7)-H(7)···S(2)'' angle [161.1°] is compatible with the presence of a hydrogen bond.

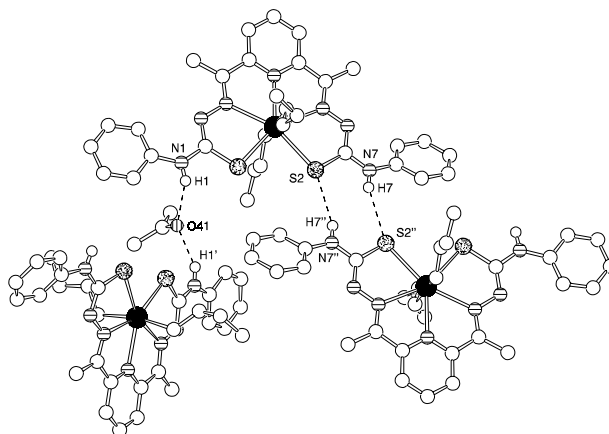


Figure 2. Representation¹⁴ of the crystal structure of [ⁿBu₂Sn(dappt)]·(Me₂CO)_{0.5} (**3**), showing three molecules of the tin complex and one of the acetone solvate. The dashed lines show the possible hydrogen bonds. Except for H(1) and H(7) all other hydrogen atoms are omitted for the sake of clarity.

Infrared spectroscopy

The main vibrational bands of H₂dappt and of its complexes are shown in Table 3. The high frequency bands of the uncomplexed ligand, centered at 3354, 3321 and 3214, 3114 cm⁻¹, are attributed to ν(N-H) stretching vibrations. The disappearance of the latter two absorptions upon complexation is a consequence of the double deprotonation of the H₂dappt ligand. The absence of large systematic shifts of the ν(N-H) mode indicates that this absorption is best assigned to the ν(PhN-H) vibration. Significant changes in the ligand bands upon complexation include variations in the ν(C=N, C=C) vibration energies and systematic shifts of the ν(C=S) absorptions bands to lower frequencies. These data indicate coordination through the azomethine nitrogen, the pyridine nitrogen and the sulfur atoms¹.

Mössbauer spectroscopy

The ^{119}Sn Mössbauer data for the complexes are reported in Table 4, which includes parameters from the literature for comparison. All complexes present one heptacoordinated Sn(IV) central atom in a distorted pentagonal bipyramidal configuration (PBP), with the SNNNS donor atoms in the pentagonal plane and the two other groups (R, Cl) in the axial positions.

Isomer shifts

The isomer shifts (δ) of complexes **1** (0.89 mm s $^{-1}$) and **5** (0.97 mm s $^{-1}$) are lower than that of the parent acid MeSnCl_3 (1.20 mm s $^{-1}$)¹⁵. The same can be seen for complexes **2** (1.42 mm s $^{-1}$) and **6** (1.41 mm s $^{-1}$); **3** (1.43 mm s $^{-1}$) and **7** (1.63 mm s $^{-1}$); **4** (1.28 mm s $^{-1}$), **8** (1.21 mm s $^{-1}$) and **9** (1.22 mm s $^{-1}$), compared to their parent acids Me_2SnCl_2 (1.49 mm s $^{-1}$), $n\text{Bu}_2\text{SnCl}_2$ (1.75 mm s $^{-1}$)¹⁶ and Ph_2SnCl_2 (1.32 mm s $^{-1}$), respectively.

In general, isomer shifts decrease upon complexation as a result of rehybridization of the Sn atoms in complexes with a greater involvement of Sn(IV) d-orbitals, thus reducing the s-character in the overall hybridization of the metal^{17,18}.

The complexes having the same Sn(IV) precursor with different ligands, *i.e.*, **2** and **6**, show very similar isomer shifts. This can be explained by considering that the only difference between the ligands consists in the thioamide

nitrogen atoms, N(1) and N(7) which are attached to a phenyl group in H_2dappt and to a hydrogen atom in H_2daptsc , respectively. As this difference is outside the coordination sphere of the Sn(IV) atom, no sensible change in the s-electron density of Sn(IV) nucleus is expected.

On the other hand, the considerable increase in the isomer shift of complex **7** (1.63 mm s $^{-1}$) as compared to complex **3** (1.43 mm s $^{-1}$) may be related to the presence of a Me_2CO molecule in **3** and two Cl^- counter ions in **7**, which are less electronegative than the oxygen atom. This accounts for the higher δ of **7** as compared to **3** as a consequence of the inverse dependence of isomer shift with electronegativity¹⁵.

On going now from **1** (0.89 mm s $^{-1}$) to **4** (1.28 mm s $^{-1}$), one sees that the ligand remains unchanged, but the Cl^- was replaced by an alkyl group and the isomer shift of **4** increases in relation to **1**. This result is also consistent with the inverse dependence of δ with the electronegativity of the bonded atoms at the Sn(IV) center.

Quadrupole splitting

From the quadrupole splitting (Δ) values, presented in Table 4, it is not possible to characterize Sn(IV) complexes as being tetra-, penta-, hexa-, or heptacoordinated^{15,19,20}. However, a semiquantitative relationship of the Mössbauer quadrupole splitting (Δ) and the R-Sn-R angle has been reported for a series of distorted heptacoordinated diorganotin(IV) derivatives^{15,19,20} by the equation

Table 3. Main IR bands (cm $^{-1}$) for H_2dappt and its Sn(IV) complexes.

Compound	$\nu(\text{N-H})$	$\nu(\text{C=N, C=C})$	$\nu(\text{C-S}) + \nu(\text{C-N})$	$\nu(\text{C-S})$
H_2dappt	3337, 3321, 3214, 3114	1597, 1546, 1511, 1448	1354	814
1 [$\text{MeSnCl}(\text{dappt})$]	3375, 3320 - -	1594, 1561, 1521, 1493	1316	690
2 [$\text{Me}_2\text{Sn}(\text{dappt})$]	3375, 3326 - -	1594, 1553, 1532, 1497	1308	694
3 [$n\text{Bu}_2\text{Sn}(\text{dappt})$] $\cdot(\text{Me}_2\text{CO})_{0.5}^*$	- 3328 - -	1590, 1544, 1519, 1476	1310	691
4 [$\text{Ph}_2\text{Sn}(\text{dappt})$]	- 3363 - -	1600, 1558, 1527, 1474	1317	693

* $\nu(\text{C=O}) = 1695 \text{ cm}^{-1}$

Table 4. Mössbauer data and C-Sn-C angles ($^\circ$) for heptacoordinated *bis*(thiosemicarbazones) complexes.

Complex	δ (mm s $^{-1}$)	Δ (mm s $^{-1}$)	C-Sn-C(obs.)	C-Sn-C(calc.)
1 [$\text{MeSnCl}(\text{dappt})$] ^a	0.89(1)	1.58(1)	-	-
2 [$\text{Me}_2\text{Sn}(\text{dappt})$] ^a	1.42(1)	3.86(1)	-	177 ^f
3 [$n\text{-Bu}_2\text{Sn}(\text{dappt})$] $\cdot(\text{Me}_2\text{CO})_{0.5}^a$	1.43(1)	3.51(1)	168.1	165 ^f
4 [$\text{Ph}_2\text{Sn}(\text{dappt})$] ^a	1.28(1)	3.29(1)	-	168 ^g
5 [$\text{MeSnCl}(\text{Hdaptsc})$] $\cdot\text{Cl}\cdot\text{MeOH}^b$	0.97(1)	2.16(1)	165.7	-
6 [$\text{Me}_2\text{Sn}(\text{daptsc})$] ^c	1.41(1)	3.58(1)	-	167 ^f
7 [$n\text{-Bu}_2\text{Sn}(\text{H}_2\text{daptsc})$] $\cdot\text{Cl}_2\cdot\text{MeNO}_2^d$	1.63(1)	4.05(1)	176.3	170 ^f
8 [$\text{Ph}_2\text{Sn}(\text{Hdaptsc})$] $\cdot\text{Cl}^e$	1.21(1)	3.13(1)	167.9	174 ^g
9 [$\text{Ph}_2\text{Sn}(\text{daptsc})$] $\cdot 2\text{DMF}^c$	1.22(1)	2.84(1)	166.9	167 ^g

H_2dappt = 2,6-diacetylpyridine *bis*(4-phenylthiosemicarbazone), H_2daptsc = 2,6-diacetylpyridine *bis*(thiosemicarbazone), H_2daps = 2,6-diacetylpyridine *bis*(salicyloylhydrazine), ^aThis work, ^bRef. 15, ^cRef. 1, ^dRef. 2, ^eRef. 3, ^fCalculated using [alkyl] = - 0.97 mm s $^{-1}$, ^gCalculated using [Ph] = - 0.77 mm s $^{-1}$.

$|\Delta| = 4[R](1-3/4\sin^2\theta)^{1/2}$, where θ is the R-Sn-R angle and $[R]$ is the partial quadrupole splitting of the R group.

Considering complexes **3** and **7**, whose structures were determined by single crystal diffraction, the $[^n\text{Bu}]$ can be estimated. Inserting the values $\Delta = 3.51 \text{ mm s}^{-1}$ and $\theta = 168^\circ$ for complex **3** and $\Delta = 4.05 \text{ mm s}^{-1}$ and $\theta = 176^\circ$ for complex **7** in the above equation, the following values are obtained for $[^n\text{Bu}] = -0.91 \text{ mm s}^{-1}$ and -1.00 mm s^{-1} , respectively (average value $= -0.95 \text{ mm s}^{-1}$), which are in excellent agreement with the -0.97 mm s^{-1} value for $[\text{alkyl}]$ ¹⁹. Now, using $[\text{alkyl}] = -0.97 \text{ mm s}^{-1}$, R-Sn-R angles of 177° and 167° , respectively, are predicted for complexes **2** and **6**.

From the $[\text{Ph}]$ values of complexes **8** (-0.80 mm s^{-1})³, **9** (-0.74 mm s^{-1}) and $[\text{Ph}_2\text{Sn}(\text{dapa})]$ (-0.78 mm s^{-1})¹⁹, where $\text{H}_2\text{dapa} = 2,6\text{-diacetylpyridine bis}(2\text{-aminobenzoyl-hydrazone})$, an estimated value for $[\text{Ph}]$ in similar heptacoordinated organotin(IV) complexes of -0.77 mm s^{-1} is obtained. By inserting Δ (3.29 mm s^{-1}) for **4** and $[\text{Ph}] = -0.77 \text{ mm s}^{-1}$ into the equation, the Ph-Sn-Ph angle is calculated to be 168° .

Acknowledgments

The authors are grateful to *Prof. Dr. J. Strähle* for the possibility of data collection for the crystal structure determination, and to CNPq and FAPEMIG in Brazil for financial support.

Supplementary Information

Crystallographic data (excluding structural factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 138942. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

1. Casas, J. S.; Castiñeiras, A.; Sánchez, A.; Sordo, J. Vásques-Lópes, A.; Rodríguez-Arquielles, M. C.; Russo, U. *Inorg. Chim. Acta* **1994**, *221*, 61.
2. De Sousa, G. F.; Valdéz-Martínez, J.; Abras, A.; Filgueiras, C. A. L. Unpublished results.
3. Moreno, P. C.; Francisco, R. H. P.; Gambardella, M. T. do P.; De Sousa, G. F.; Abras, A. *Acta Cryst.* **1997**, *C53*, 1411.
4. Bino, A.; Cohen, N. *Inorg. Chim. Acta* **1993**, *210*, 11.
5. Toukhy, A. *Inorg. Chim. Acta* **1991**, *180*, 85.
6. Casas, J. S.; Sánchez, A.; Sordo, J.; Vásques-Lópes, A.; Castellano, E. E.; Zukerman-Schpector, J.; Rodríguez-Arquielles, M. C.; Russo, U. *Inorg. Chim. Acta* **1994**, *216*, 169.
7. Iskander, M. F.; Labib, L.; Nour El-din, M. M. Z.; Tawfik, M. *Polyhedron* **1989**, *23*, 2755.
8. Offiong, O. E. *Transition Met. Chem.* **1997**, *22*, 263.
9. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
10. Spek, A. L.; PLATON, Program for the Treatment of Crystallographic Data, University of Utrecht, Holland, 1996.
11. Sheldrick, G. M.; SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
12. Sheldrick, G. M.; SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
13. Vinogradov, S. N.; Linnel, R. A. *Hydrogen Bonding*, Van Nostrand Reinhold, New York, 1971, 176.
14. Keller, E.; SCHAKAL92, Program for Graphical Representation of Molecular Models, University of Freiburg, Germany, 1992.
15. De Sousa, G. F.; Filgueiras, C. A. L.; Abras, A.; Aljuaid, S. S.; Hitchcock, P. B.; Nixon, J. F. *Inorg. Chim. Acta* **1994**, *218*, 139.
16. Davies, A. G. *Chem. Brit.* **1968**, 403.
17. Randall, R. S.; Wedd, R. W. J.; Sams, R. J. *J. Organomet. Chem.* **1971**, *30*, C19.
18. Cunningham, D.; Little, M.; McLoughlin, K. *J. Organomet. Chem.* **1979**, *165*, 287.
19. Carini, C.; Pelizzi, G.; Tarasconi, P.; Pelizzi, C.; Molloy, K. C.; Waterfield, P. C. *J. Chem. Soc., Dalton Trans.* **1989**, 289.
20. De Sousa, G. F.; Mangas, M. B. P.; Francisco, R. H. P.; Gambardella, M. T. do P.; Rodrigues, A. M. G. D.; A. Abras. *J. Braz. Chem. Soc.* **1999**, *10*, 222.

Received: March 22, 2000

Published on the web: May 17, 2001